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(71)Applicant : TOYOHASHI UNIVERSITY OF TECHNOLOGY.

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(72)Inventor : FUJIE KOICHI
DAIMON HIROYUKI
SAEKI TAKASHI

(54) METHOD FOR DECOMPOSING WATER-SOLUBLE POLYMER, METHOD FOR RECYCLING THE SAME AND METHOD FOR ORGANIC SYNTHESIS USING SUPERCRITICAL WATER OR SUBCRITICAL WATER AS REACTION SOLVENT

(57)Abstract:

PROBLEM TO BE SOLVED: To recover an industrially useful organic compound by decomposing a polyvinyl alcohol discharged to the environment under the present situation.
SOLUTION: A polyvinyl alcohol is decomposed by using critical water or subcritical water at 200–450° C under 4–45 MPa to recover benzaldehyde, acetophenone or benzophenone being an industrially useful organic compound.

LEGAL STATUS

[Date of request for examination] 18.09.2000

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[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

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CLAIMS

[Claim(s)]

[Claim 1] The decomposition approach of the water soluble polymer characterized by disassembling a water soluble polymer, using supercritical water or subcritical water as a reaction solvent.

[Claim 2] The decomposition approach of the water soluble polymer according to claim 1 characterized by said water soluble polymer being polyvinyl alcohol.

[Claim 3] The decomposition approach of the water soluble polymer according to claim 1 characterized by using the temperature of 200-450 degrees C, the supercritical water of pressure 4-45MPa, or subcritical water.

[Claim 4] The recycle approach of the water soluble polymer characterized by disassembling a water soluble polymer, using supercritical water or subcritical water as a reaction solvent, and collecting useful organic compounds industrially.

[Claim 5] The recycle approach of the water soluble polymer according to claim 4 characterized by for said water soluble polymer being polyvinyl alcohol, and said organic compound collected being a benzaldehyde, an acetophenone, or a benzophenone.

[Claim 6] supercritical water or subcritical water -- a reaction solvent -- carrying out -- a water soluble polymer -- since -- the organic synthesis approach using the supercritical water or subcritical water characterized by compounding a useful organic compound industrially as a reaction solvent.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the approach of disassembling the water soluble polymer discharged in the environment, and collecting useful organic compounds industrially.

[0002]

[Description of the Prior Art] In recent years, the matter which is hard to disassemble during industrial wastewater biologically is being contained more often with diversification of the production process of an industrial field. For example, polyvinyl alcohol (PVA) is one of the high water soluble polymers of versatility used in many fields, such as Vynylon fiber, textile finishing, a paper processing agent, a film raw material, adhesives, an emulsification distribution stabilizer, and a home wash paste. The wastewater containing PVA has a very high COD value compared with a BOD value, and hardly shows biodegradability. The present condition is having only diluted PVA, or having performed and discharged other mixed processings, since the COD value's is not regulated in the effluent standard in current Water Pollution Control Law. If PVA content wastewater continues being emitted as it is, we are anxious about spreading and accumulating in a nature. Since processing of PVA content wastewater cannot respond only by biological treatment, combination processing with biological treatment and physicochemical processing is considered using physicochemical processing.

[0003] The Fenton oxidation style using OH radical which has powerful oxidizing power as a chemical preparation method is studied from improvement in the treatment effect of refractory organic substances, an improvement of biodegradability, etc. being expected. However, an acid reagent is used for this approach in large quantities, and it has a problem of the processing time being long and a lot of sludges making it generate.

[0004] On the other hand, since the supercritical water in the condition more than the critical point (374 degrees C, 22MPa) shows high reactivity, research of decomposition and defanging of deleterious material, oil-sizing of plastics, etc. is done using this. Moreover, research for the subcritical water below the critical point to collect useful compounds from trash industrially by using this as a reaction solvent, since an ionic product is high and reactivity is low compared with supercritical water is done.

[0005] For example, the research which EPDM rubber is made to react with supercritical water, and is liquefied is made. It is reported that liquefaction of EPDM rubber becomes max near 430 degree C, and generation of a hypoviscosity product advances in the field where a dielectric constant is low. Under the hydrothermal conditions of low-temperature high pressure, it is also reported that it can desulfurize since the sulfur and the zinc oxide which are added by EPDM rubber as a vulcanizing agent react and all sulfur precipitates as zinc sulfide. Moreover, if polyethylene terephthalate (PET) is made to react by supercritical underwater, it is also reported that 95% of PET cracking severity and 50% of oligomer yield are obtained in 2 minutes, and the terephthalic acids which are PET synthetic powder are collected at 99.5% or more of purity. However, a report of the processing of PVA by elevated-temperature high-pressure water is not seen.

[0006]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the approach of disassembling the water soluble polymer discharged in the environment, and collecting useful organic compounds industrially.

[0007]

[Means for Solving the Problem] The decomposition approach of the water soluble polymer of this invention is characterized by disassembling a water soluble polymer (PVA), for example, polyvinyl alcohol, using supercritical water or subcritical water as a reaction solvent. As for the conditions of supercritical water or subcritical water, in this invention, it is desirable to be referred to as the temperature of 200–450 degrees C and pressure 4–45MPa.

[0008] The recycle approach of the water soluble polymer of this invention disassembles a water soluble polymer (PVA), for example, polyvinyl alcohol, using supercritical water or subcritical water as a reaction solvent, and is characterized by collecting organic compounds, such as a useful benzaldehyde and a useful acetophenone, and a benzophenone, industrially.

[0009] moreover, this invention -- supercritical water or subcritical water -- a reaction solvent -- carrying out -- a water soluble polymer -- since -- the organic synthesis approach which compounds a useful organic compound industrially is offered.

[0010]

[Embodiment of the Invention] First, supercritical water and subcritical water are explained. There are three conditions, a solid-state, a liquid, and a gas, in the matter. If temperature and a pressure are raised gradually and a certain specific pressure and temperature (critical point) are exceeded from the condition that the gas and the liquid are mixed, the interface of a gas and a liquid disappears and the range which maintains the condition of a fluid exists. Such a fluid is called supercritical fluid and it becomes a gas and the fluid of high density with the middle property of a liquid. That is, it has a high fluidity like a gas at the same time it dissolves various matter like a liquid.

[0011] The critical points of water are the temperature of 374 degrees C, and pressure 221 atmospheric pressure, and supercritical water means the elevated-temperature high-pressure water in the temperature and the pressure condition beyond the critical point. Moreover, subcritical water means the elevated-temperature high-pressure water in the temperature and the pressure condition below the critical point.

[0012] Depending on temperature and a pressure, as for supercritical water; values, such as a consistency, viscosity, a dielectric constant, an ionic product, and a diffusion coefficient, change continuously. It is known that the solubility which becomes important as a reaction solvent will become large with increase of a consistency. About solubility, a dielectric constant is also an important element, and a dielectric constant becomes large with increase of a consistency, and decreases along with the rise of temperature. With usual water, to a dielectric constant being about 80, since a dielectric constant falls to about 2 at 500 degrees C, the property of the nonpolar matter is shown, and it mixes also with inorganic gas, such as a nonpolar organic substance and oxygen, and air, to homogeneity completely, and suits with supercritical water. Thus, supercritical water is served as nonpolar matter.

[0013] In subcritical underwater one, an ionic product $kw ([H^+], [OH^-])$ increases with temperature and a pressure, and it increases also thousands times under 5×10 to about 10, and ordinary temperature ordinary pressure at 300 degrees C. This does not need an additive but shows that it can hydrolyze only with water. Especially, at a reaction in an autoclave, a hydrolysis reaction is most promoted the bottom of maximum vapor tension, and around 300 degrees C. Moreover, since it is in the condition which a gaseous phase and the liquid phase are mixing, as for saying [the bottom of maximum vapor tension], it turns out that a hydrolysis reaction has priority in the liquid phase, and radical reaction has priority in a gaseous phase.

[0014] In this invention, the polyvinyl alcohol which is a water soluble polymer is disassembled, using the supercritical water or subcritical water which is elevated-temperature high-pressure water which has the above properties as a reaction solvent. Furthermore, it came to complete a header and this invention for a useful organic compound being industrially [a benzaldehyde an acetophenone, a benzophenone, etc.] recoverable by decomposition of PVA.

[0015] In this invention, as for the conditions of supercritical water or subcritical water, it is

desirable to be referred to as the temperature of 200–450 degrees C and pressure 4–45MPa, and they are more desirable. [of especially the temperature of 280–400 degrees C and the range of pressure 6–35MPa]

[0016]

[Example] Hereafter, the example of this invention is explained.

[0017] The experiment was presented with what dissolved PVA (polymerization degree 1800 [about], about 88% of the degrees of saponification) in pure water. PVA concentration in a sample was made into 1% supposing waste industrial waters.

[0018] The batch process reactor (proof-pressure glass industry, TSC-006 mold) used for the experiment at drawing 1 is shown. The reaction container 2 which taught and sealed the sample in the salt bath 1 set as predetermined temperature is immersed, and a reaction is made to start, as shown in drawing 1. The reaction container 2 consists of Hastelloy (trademark) which is a nickel-Cr-Mo alloy, and the volume is 3 66cm. The heat-resistant temperature of this reaction container 2 is about 450 degrees C, and pressure-proofing is about 45 MPa(s). The pressure in the reaction container 2 was measured with the pressure gage 3, and the temperature in the reaction container 2 was guessed from the pressure value. Consequently, it turned out that laying temperature is reached in about 7 – 8 minutes. The reaction container 2 was cooled with water after predetermined time progress, and the reaction was stopped. The reaction temperature and reaction pressure which were set as the following table 1 are shown.

[0019]

[Table 1]

反応温度 [°C]	200	250	280	300	350	400
反応圧力 [MPa]	1.5	3.9	6.1	8.4	17.1	33.8

[0020] The samples after a reaction halt and in a reaction container were collected. About the liquid phase, analysis of gel permeation chromatography (GPC) and an organic acid was performed. Moreover, qualitative quantitative analysis by GC-MS was carried out about the hexane extractable material from the liquid phase. About solid content, qualitative quantitative analysis by GC-MS was similarly carried out after the extract.

[0021] Aging of the organic carbon concentration in each reaction condition (280 degrees C, 300 degrees C, 350 degrees C, 400 degrees C) is shown in drawing 2 – drawing 5. Although not illustrated, generation of a solid was not able to be checked at 200 degrees C or 250 degrees C. At 280–350 degrees C, the inclination which the amount of generation of a solid increases was seen as temperature became high. At 400 degrees C, compared with 350 degrees C, there were few amounts of generation of a solid and the result that there was much soluble organic carbon was obtained. From this, a solid generates first by decomposition of PVA and it is thought that a solid decomposes further after that.

[0022] The effect of the reaction temperature and time amount which are given to pH of a reaction solution at drawing 6 is shown. The inclination for pH to fall for a short time was seen, so that reaction temperature was high. pH colored 3.6 or less solution yellow, and the inclination for pH to become muddy or less in 3.2 further was seen. In the reaction solution, it was checked that an acetic acid, formic acid, and carbonic acid are generating. The amount of generation of an acetic acid increased with temperature below 300 degrees C, and became fixed above 350 degrees C. Generation of formic acid and carbonic acid was checked above 350 degrees C.

[0023] It is thought that the solid which the acetic-acid radical of PVA ****ed below 300 degrees C first, and the acetic acid generated, and then was PVA(ed) or generated from these results decomposes, and formic acid and carbonic acid generate.

[0024] From GPC analysis of a 300-degree C reaction solution, it was checked that the peak of PVA falls with reaction time. The same result was obtained also in other reaction temperature. Moreover, after the reaction, since the peak which has absorption in an ultraviolet region (243nm) had appeared, generation of a ring compound was suggested.

[0025] As a result of analyzing the product and solid in the liquid phase by GC-MS, the

benzaldehyde, the acetophenone, and the benzophenone were checked. Each product was proportional to the amount of a solid, and there were most amounts of generation on 300 degrees C and the conditions for 30 minutes. benzaldehyde: -- acetophenone: -- the generation ratio of a benzophenone was 25:12:1. These organic compounds are useful as a raw material of various chemicals.

[0026] In the conventional knowledge, when PVA is pyrolyzed in about 500-degree C gaseous phase, for example, it is clear that a benzaldehyde is obtained. Also in the elevated-temperature high-pressure underwater which is the reaction environment of this invention, cyclization takes place by radical-reactions, such as desorption of the side chain of PVA, and a pyrolysis, and it is expected that the above aromatic compounds generate.

[0027]

[Effect of the Invention] As explained in full detail above, according to this invention, a useful organic compound is industrially recoverable by decomposing PVA, using supercritical water or subcritical water as a reaction solvent.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the approach of disassembling the water soluble polymer discharged in the environment, and collecting useful organic compounds industrially.

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PRIOR ART

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[0004] On the other hand, since the supercritical water in the condition more than the critical point (374 degrees C, 22MPa) shows high reactivity, research of decomposition and defanging of deleterious material, oil-izing of plastics, etc. is done using this. Moreover, research for the subcritical water below the critical point to collect useful compounds from trash industrially by using this as a reaction solvent, since an ionic product is high and reactivity is low compared with supercritical water is done.

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MEANS

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degrees C. Moreover, since it is in the condition which a gaseous phase and the liquid phase are mixing, as for saying [the bottom of maximum vapor tension], it turns out that a hydrolysis reaction has priority in the liquid phase, and radical reaction has priority in a gaseous phase.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The block diagram of the batch process reactor used in the example of this invention.

[Drawing 2] Drawing showing aging of the organic carbon concentration in the sample in 280 degrees C.

[Drawing 3] Drawing showing aging of the organic carbon concentration in the sample in 300 degrees C.

[Drawing 4] Drawing showing aging of the organic carbon concentration in the sample in 350 degrees C.

[Drawing 5] Drawing showing aging of the organic carbon concentration in the sample in 400 degrees C.

[Drawing 6] Drawing showing aging of pH of a sample.

[Description of Notations]

1 -- Salt bath

2 -- Reaction container

3 -- Pressure gage

[Translation done.]

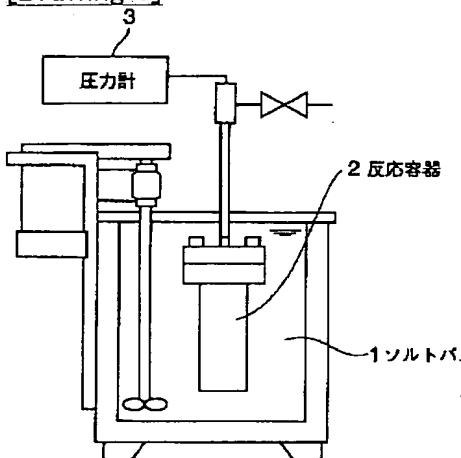
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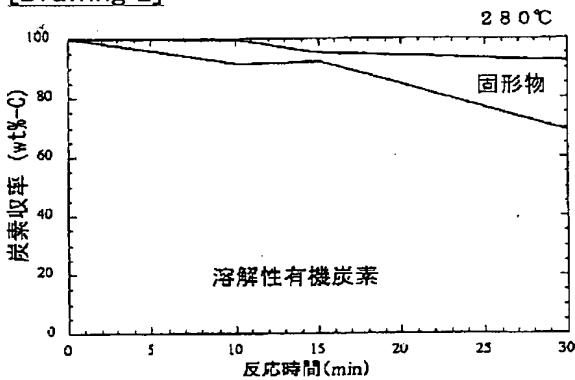
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DRAWINGS

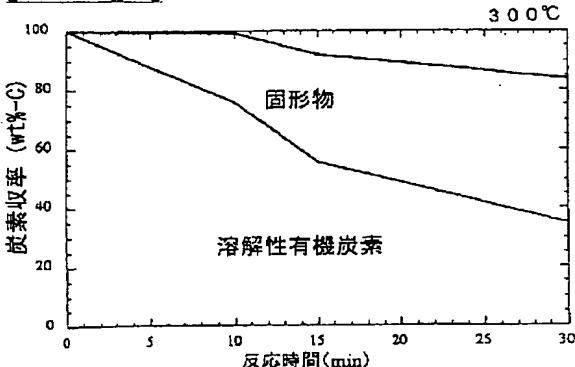
[Drawing 1]



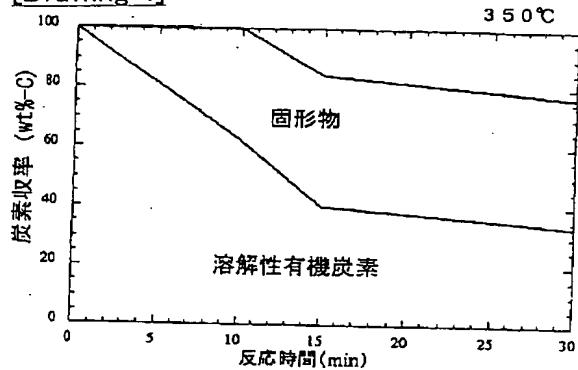
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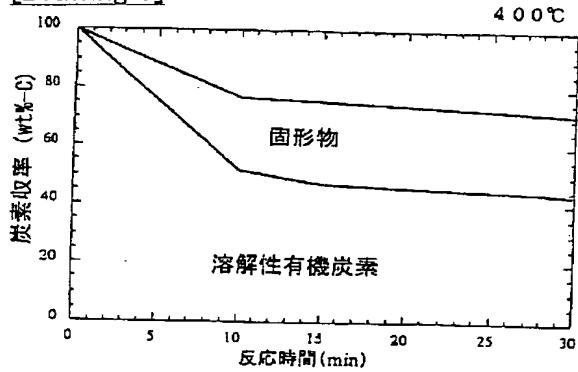
[Drawing 3]



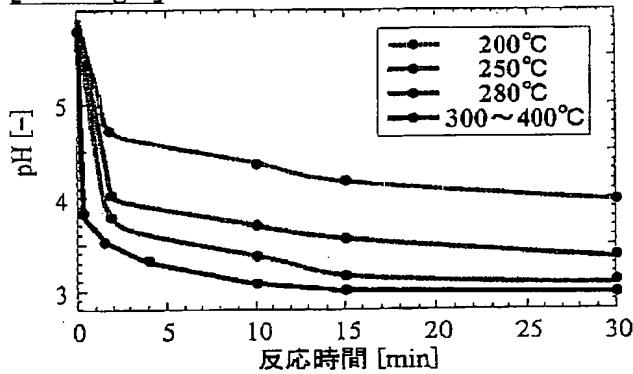
[Drawing 4]



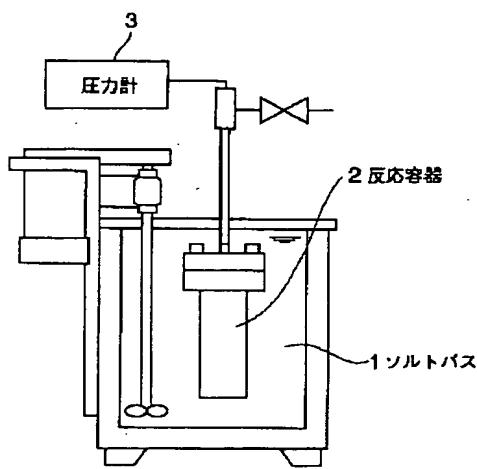
[Drawing 5]



[Drawing 6]



[Translation done.]

Drawing selection drawing 1 

[Translation done.]